I. C. 7475 September 1948

UNITED STATES
Department of the Interior
J. A. Krug, Secretary

BUREAU OF MINES
James Boyd, Director

INFORMATION CIRCULAR

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METHODS USED IN EVALUATING ADSORBENT CLAYS

BY

Staff, Tuscaloosa Branch, Metallurgical Division
Southern Experiment Station, Tuscaloosa, Ala.

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INTRODUCTION AND SUMMARY

In the course of its investigation of mineral resources, the Bureau of Mines has made a survey of methods employed in testing clays for their oil-clarifying or bleaching capacities. The initial purpose of the presentation is to describe the procedures and apparatus that are accepted as standard by the industry. Other methods that have been found particularly suitable for the clay laboratory also are described.

This information circular is one of a series dealing with testing of clays and is designed to form a section or unit of Part II, Syllabus of Clay Testing.[2]

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[1] The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Information Circular 7475."

[2] Klinefelter, T. A., et al, Syllabus of Clay Testing, Part I: Bureau of Mines Bull. 451, 1943, 35 pp.

In making the survey, it was found that the oil industry and the producers of adsorbent clays usually employ one of two methods for testing bleaching qualities. The two methods were developed from the two different procedures, "percolation" and "contact," that the oil industry employs in clarifying its oil stocks. The test methods, adjusted to the process and oil stocks used in the refinery, are laboratory duplications of the clarification conditions.

In laboratories engaged in testing all types of clays for their various uses it is not necessary to carry out the testing with the detail required in the oil industry. It has been found adequate to evaluate the unknown clay or clays against a single standard clay and a single standard oil stock. Moreover, much simpler equipment may be used. The Federal Geological Survey adopted a method of this type some years ago, and the Bureau of Mines has recently developed another that is believed to be somewhat more accurate. In studying the possibilities of such a single method, the Bureau of Mines also worked out a modification of one of the industrial methods that appears to have considerable merit for industrial use.

ACKNOWLEDGMENTS

This report is one of many on various aspects of the Federal Bureau of Mines program directed toward the more effective utilization of our mineral resources. These investigations are conducted by the Mining Division, L. B. Moon, chief, and by the Metallurgical Division, O. C. Ralston, chief.

The scope of the report falls in the province of the Metallurgical Division. The work was carried out at the Tuscaloosa Branch, W. H. Coghill, former chief, H. G. Iverson, present chief, and T. A. Klinefelter, in charge of the clay laboratory, and in cooperation with the University of Alabama.

The staff engaged in the work included William W. Good, S. J. Broderick, E. S. Hertzog, E. R. Todd, D. W. Ross, H. P. Hamlin, and T. A. Klinefelter.

The staff is particularly indebted to the Filtrol Corporation of Los Angeles, Calif., and to the Attapulgus Clay Co. of Philadelphia, Pa., for supplying detailed drawings and instructions concerning their standard testing methods, also to the American Oil Chemists Society Chicago, Ill.

This staff article was prepared by T. A. Klinefelter.

REFERENCES

In this presentation, a brief summary only is given as to the geological history, geographic distribution, and general properties of the adsorbent clays. There is considerable literature on these clays, and for more detailed information the following references should be consulted. They are comprehensive, and all contain bibliographies covering all phases quite thoroughly. All have been drawn from freely for some of the discussion in the present paper.

1. Nutting, P. G., Adsorbent Clays, Their Distribution, Properties, Production, and Uses: Geol. Survey Bull. 928C, 1943, pp. 127-221.

2. Ross, C. S., and Hendricks, S. B., Minerals of the Montmorillonite Group, Their Origin and Relation to Soils and Clays: Geol. Survey Prof. Paper 205-B, 1945, pp. 23-79.

3. Davis, C. W., and Vacher, H. C. (revised by Conley, J. E.), Bentonite: Its Properties, Mining, Preparation, and Utilization: Bureau of Mines Tech. Paper 609, 1940, 83 pp.

For those interested in following the methods employed by the industry in more detail than could be presented in this report, the following references should be consulted:

1. Official and Tentative Methods of the American Oil Chemists' Society, 35 East Wacher Drive, Chicago, Ill. It should be noted that standard samples of fuller's earth may be obtained from the society.

2. Adsorbent Testing and its Application to Refining Problems: Research and Development Department, Attapulgus Clay Co., 210 W. Washington Square, Philadelphia 5, Pa.

3. Filtrol Adsorbents in the Finishing of Petroleum Oil Stocks: Filtrol Corporation, 634 South Spring St., Los Angeles, Calif.

Part 1. OIL-BLEACHING CLAYS

Description and Origin

This report deals only with the class of adsorbent clays used commercially by the oil industry. Many other materials and clays have bleaching powers but have not been found to be of much importance commercially.

At the present time, the oil-adsorbent clays are largely of two main types - the fuller's earths of Georgia and Florida and a certain type of bentonite found in Mississippi, Arizona, and California.

The fuller's earths are a rather distinct class of clays and have been in use as adsorbents of one sort or another for centuries. For oil clarification they need little treatment other than drying and screening. About half the oil clarification in this country is carried out by means of the fuller's earths.

The geologic origin of the fuller's earths has in the past been obscure and attributed to various rock decompositions. In recent years, however, there has been a growing opinion that the fuller's earths are very old and very much altered volcanic ash beds. If so, then they logically are a group of the bentonites. The idea is based mainly on the facts that the fundamental clay mineral is one of the several montmorillonite clay minerals (saponite), and that virtually all the montmorillonites are from volcanic ash. However, no volcanic shards are found, and the replaceable base is usually magnesium. On the other hand, those montmorillonites that are traceable to ash beds usually have calcium, sodium, or potassium as the main replaceable base, and volcanic shards are invariably present. Nevertheless, the volcanic-ash origin of fuller's earth seems to fit the general facts better than other theories.

The other clays employed for bleaching are generally termed "bentonites", although the same name is used to designate another group of clays of great commercial importance in other industrial fields. This confused nomenclature will be discussed hereinafter in more detail. Although the bleaching bentonites and other bentonites all have a common origin, in that they are unmistakably products of altered volcanic ash, they differ from one another decidedly in certain physical and chemical aspects.

The chief variations that appear to cause the physical differences are the replaceable bases. The bentonites employed for bleaching have calcium as the predominant replaceable base, whereas the other group of commercial importance (the swelling bentonites, as typified by those from Wyoming and the Dakotas) has sodium as the main base. In point of physical differences, the most outstanding one is water absorption. The bleaching bentonite may absorb as much as 75 percent water and show little or no increase in volume, whereas the swelling bentonites may absorb as much as 200 percent water and show volume increase of 15 or 16. When it comes to bleaching powers, there is a most decided difference. A few of the bleaching bentonites are good bleachers in the natural state, but most of them require an acid leaching to bring out their full powers. On the other hand, the swelling and other types of bentonites are not bleachers in the natural state, nor can they be made so by the acid activation. Another difference between the bleaching bentonites and the swelling type lies in the relative amount of volcanic shards contained therein. The bleaching bentonites have few and scattered shards, whereas the swelling type contains relatively large amounts, and these show less alteration. This would indicate that the high-calcium bleaching bentonites are of older origin than the high-soda swelling bentonites and occupy an intermediate position between the high-magnesian fuller's earths and the swelling bentonites.

In passing, a brief discussion of the confused nomenclature will be of interest. Clays usually receive their names from the use to which they are put, and one and the same clay may have half a dozen names, depending on who is talking. This is confusing and, within the last few years, the situation has become still more so because of the increasing tendency to employ names more in line with the technical knowledge of clays. The bleaching clays are no exception. First, there is the old trade name "fuller's earth", dating back to the time when these clays were employed in the textile trade. Next came the name "bentonite" for a clay of the swelling type that was first noticed in the Benton formation of Rock Creek, Wyo., which, therefore, was a geological nomenclature. These swelling bentonites came into wide use commercially before the high-calcium bleachers were recognized as being one of the family, and hence would seem to have some priority in the use of the name. For this reason, the clay technician is inclined to call the swelling bentonites "true bentonites." He then calls the type represented by the bleachers "metabentonites" or "subbentonites", and these latter names are beginning to be used increasingly by the industry. However, the whole family of bentonitic clays is now referred to by the clay technicians as "montmorillonites."

Perhaps it is an oversimplification to consider the three groups as separate and distinct from one another, as there is much overlapping in properties and compositions, and we find many borderline and intermediate grades. This probably explains the lack of clear correlation between bleaching properties and chemical and mineral constituents.

Commercial Use of Oil-Bleaching Clays

The use of clays for absorbent purposes, such as cleaning wool and textiles, was known to the ancients. The use as oil bleachers, however, apparently started about 100 years ago and, with the expansion of the petroleum and automobile industries, has grown at a rapid rate. In the preparation of the clays, the activation process has been in use approximately 75 years.

The clays, on being mined, are dried sufficiently so that they may be ground or otherwise prepared. For naturally active clays, such as the fuller's earths, drying and grinding may be sufficient, or the material may be processed further to produce granules or nodules of graded sizes, the degree of preparation depending on the process the consumer uses. For contact processing, a fine powder is required; whereas, for percolation clarifying, the granular or nodular form is employed.

If the clay is to be activated, the partly dried material is leached or treated several hours with hot sulfuric acid, then washed, dried, ground, and shipped. The usual product is a finely ground powder, as it will be used in the contact processing of oil.

The oil clarifying may be done in two ways, by the percolation or the contact process. In the former the clay mass acts as a filter as the oil passes, or percolates, through the granular material. In the contact process a quantity of oil is kept in intimate contact with the finely powdered clay mass for a period of time and is then filtered.

Identification

The montmorillonite-type clay can be identified positively by X-ray examination. Thermal analyses are helpful, although the presence of other minerals often tends to obscure the results. Petrographic examinations also are helpful, although the fineness of grain often makes positive analysis difficult. Certain physical characteristics are an aid, particularly the water-absorptive powers. These have been described in Part I, Syllabus of Clay Testing[3], pages 5 to 8. However, as not all montmorillonites (or bentonites, as the term is used in the trade) are bleachers, the quickest positive identification is an oil-bleaching test.

Part 2. TEST METHODS

As stated above, the tests are of two types, percolation and contact, following the two different procedures used industrially. For industrial purposes the tests must be conducted in such a manner as to permit evaluation of

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[3] Work cited in footnote 2.

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several factors aside from the decolorizing effect of the clay. Such factors are determination of the best operating conditions for any given oil stock, optimum conditions for a given stock with the individual equipment in use at the plant, control of the general plant operations, and the relative efficiencies of different absorbent clays under existing plant operations.

In evaluating clay efficiencies, several items are important, such as oil retention, calcining temperatures, filtration temperatures, weights after calcining, filter washing, time of contact or rate of percolation, and total yields. All of these items are needed for obtaining the cost data necessary for plant operation.

Contact Methods

1. Vegetable Oils

The American Oil Chemists' Society[4] has adopted the following bleaching procedure, applicable to cottonseed oil. For other oils the same apparatus is employed, but there is some difference in procedure. The official methods should be consulted for such oils.

A.O.C.S. Official Method Cc 8a-46. Bleaching Test.

Definition: This method determines the color of the sample after treatment with a specified bleaching earth under the conditions of this test.

Scope: Applicable to refined cottonseed oil.

A. Apparatus and supplies:

1. Balance, torsion type or equivalent, capacity 1,000 g. and sensitive to 0.1 g.

2. Balance weights, 0.1 to 500 g.

3. Refining cups, stainless-steel, seamless or enameled iron, with handle, 4 to 4.5 inches diameter, 4 to 4.5 inches deep, total capacity ca 900 ml.

4. Bleaching apparatus, which may be similar in design and construction to the Refining Apparatus (A.O.C.S. Official Method Ca 92-41). (See figs. 1 and 2.) The essential features of the bleaching apparatus are:

   a. T-shaped paddles constructed of a stainless steel, nickel-plated copper or brass (heavily coated) with 0.5 x 3.5-inch blade set at right angles to the shaft of the paddle.
   b. The paddles are driven at 250 ± 10 r.p.m. by any convenient means.
   c. A heat source is required that will permit heating the samples to 120° C. in not more than 5 minutes and maintaining them at not less than 105° C. Either gas or electrical heat is satisfactory.

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[4] Official and Tentative Methods of the American Oil Chemists' Society, 2d ed., 1946. Official Method Cc 8a-46.

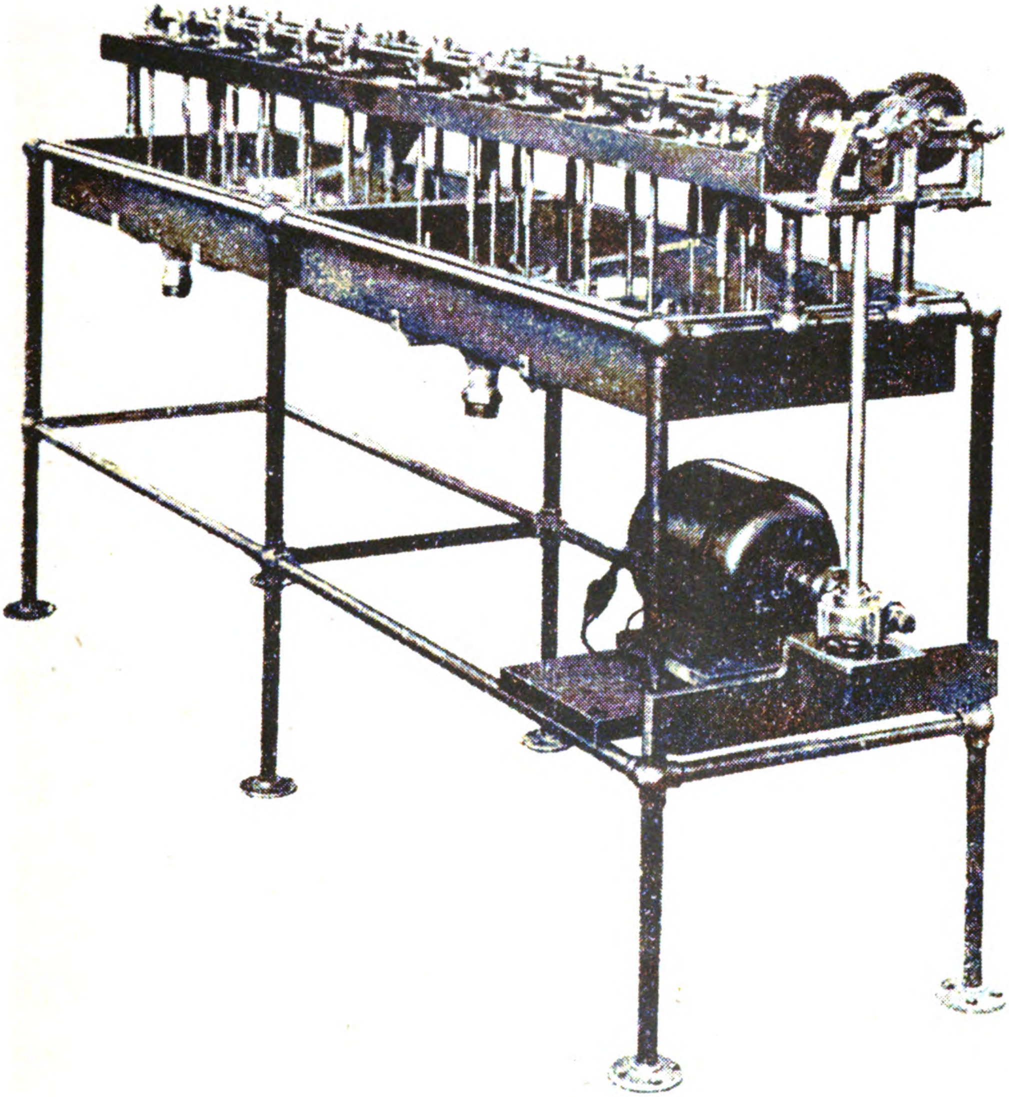

Figure 1. - Bleaching apparatus.

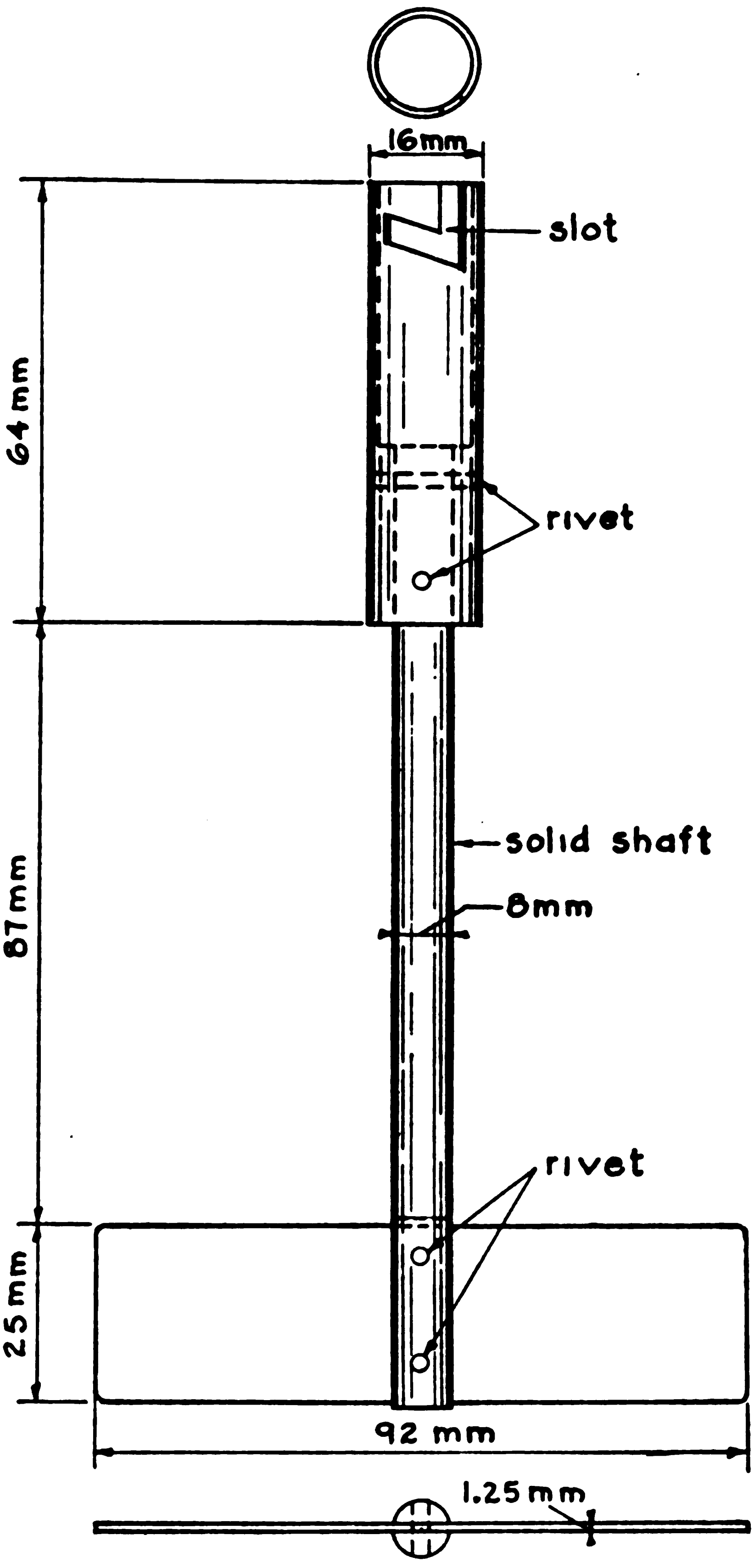

Figure 2. - Paddle for refining apparatus.

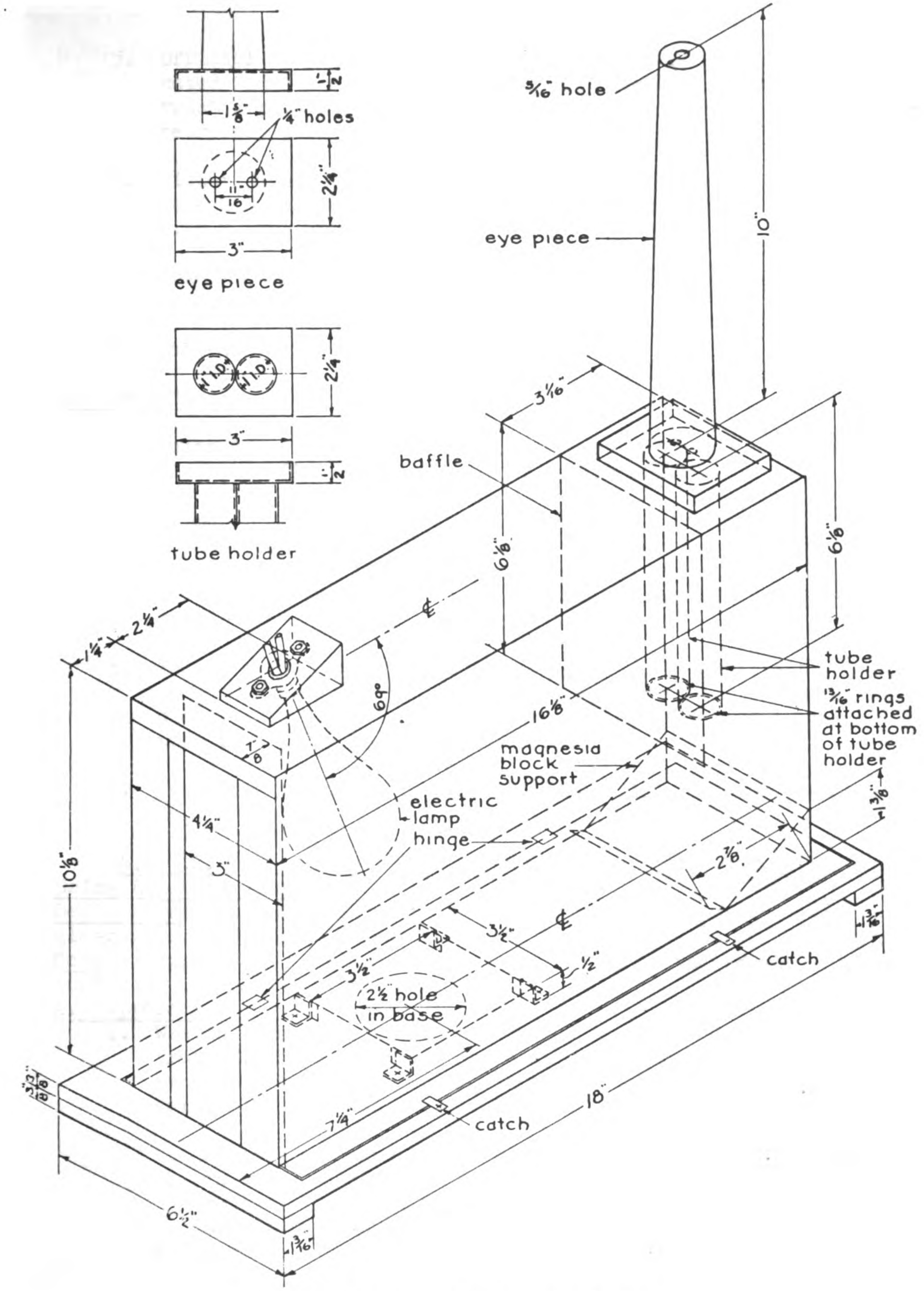

Figure 3. - Wesson-type colorimeter.

5. Official Fuller's Earth, tested and approved by the designated Committee of the American Oil Chemists' Society. A fresh supply must be obtained from the office of the secretary of the Society August 1 of each year.

6. Filter paper, 250 mm. (10-inch), of fine porosity, such as E & D No. 192, Reeve-Angel No. 871, Whatman No. 12, or S. & S. No. 596.

7. Colorimeter, color glasses, and color tubes as specified in A.O.C.S. Official Method Cc 13b-45.

8. Laboratory thermometer, 0° to 150° C.

B. Procedure:

1. Weigh 300 g. of the oil sample into refining cup. Add 6 percent (18.0 g.) of Official Fuller's Earth.

2. Commence stirring at 250 ± 10 r.p.m. and heat immediately to 120° C., requiring not more than 5 minutes. Continue stirring at the same rate for 5 minutes. Do not allow the temperature of the sample to drop below 105° C. during this period.

3. Filter through a dry filter paper. Allow a sufficient amount to pass through the filter paper to become entirely clear. Then collect a sufficient amount to fill a color tube to the 133.35 mm. etched mark.

4. Determine the color as directed in A.C.C.S. Official Method, Cc 13b-45.

A.O.C.S. Official Method Cc 13b-45. Color. Wesson Method, Using Lovibond Glasses.

Definition: This method determines the color by comparison with glasses of known color characteristics.

Scope: Applicable to all normal fats and oils, providing no turbidity is present in the sample.

A. Apparatus:

1. Wesson-type colorimeter constructed as shown in the illustration. (See fig. 3.) The instrument consists of a lightproof box with a dull-black interior, illuminated by a 100-watt, blue, frosted, Mazda, electric-light bulb.

   a. A block of magnesia 1 x 2-3/4 x 3-3/4 inches is placed in the designated location and at the proper angle to reflect the light from the electric bulb vertically upward through the color tube and color glasses.

   b. The eye piece is finished with a dull-black interior and fits over (outside) the rectangular top of the tube holder, so that the light passes through the color tube and color glasses. Eye pieces with split fields are not permitted.

c. The tube holder (1 inch i.d.) is fitted with 13/16 i.d. rings at the bottom. One ring is to retain the color tube containing the oil sample, and the other is to permit an equal amount of light to reach the color glasses.

d. The Stevenson colorimeter (see note 3) conforms to these specifications and is approved. This instrument contains a magazine for holding the color glasses, thus minimizing breakage, soiling, and scratching.

2. The colorimeter is maintained in a booth or cabinet not less than 40 inches wide and 30 inches deep. The booth or cabinet is closed, so that no external light can enter. The inside of the booth is painted a dull neutral grey of Munsell value 4.

The booth is illuminated by a 15-watt daylight bulb mounted 48 inches above the colorimeter box in an indirect fixture, so that no direct rays strike the colorimeter or the eye of the reader. The level of illumination in the booth, at top of the box of the colorimeter, is to be not less than one nor more than five foot candles.

3. Color glasses, red and yellow, of suitable numbers to match the color of the oils to be examined. Red glasses must be standardized by the U. S. Bureau of Standards (Washington, D. C.) or the Electrical Testing Laboratories (East End Ave. and 79th St., New York, N. Y.). Glasses above 1.0 red need not have the exact value shown in the table below. The minimum standard set consists of the following numbers of red and yellow glasses:

Red: 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9
1.0 2.0 2.5 3.0 3.5 4.0 5.0 6.0 7.0
7.6 8.0 9.0 10.0 11.0 12.0 16.0 20.0

Yellow: 1.0 2.0 3.0 5.0 10.0 15.0 20.0 35.0 50.0 70.0

Caution: Keep the color glasses clean and free from oil film. Handle carefully and protect against acquiring scratches. It is especially important that every color glass used be clean at the time of use.

4. Color tubes of clear, colorless glass with a smooth, flat, polished bottom and of the following dimensions: length 154 mm. over all, inside diameter 19 mm., outside diameter 22 mm. The color tubes are provided with two etched marks, one to indicate an oil column of 133.35 mm. (5.25 inches) and another to indicate an oil column of 25.4 mm. (1 inch).

5. Filter paper, fine porosity such as Eaton & Dikeman No. 192, Whatman No. 12, Reeve-Angel No. 871 or S. & S. No. 596.

B. Procedure:

1. The sample must be absolutely clear; if not, filter through a specified paper (see A, 5) at the temperature designated for reading.

2. Fill a color tube with the sample to the 133.35 mm. etched mark. Adjust the temperature to 22° ± 2° C. and read at this temperature. If the sample is not completely liquid at 22° ± 2° C., heat to a temperature of not more than 10° C. above the point of complete melting (see Note 2).

3. Place the tube containing the sample in the colorimeter and place alongside of it such red and yellow glasses (see paragraphs a and b) as are necessary to match the brightness of the oil, observing the colors of the oil and glasses through the eyepiece.

   a. Refined oil. Use only 1 yellow glass, 35 yellow for refined cottonseed oil and refined peanut oil, 70 yellow for refined soybean oil. Use not more than 2 red glasses up to and including 13.0 red, and not more than 3 red glasses above 13.0 red.

   b. Refined and bleached oil. The ratio of yellow to red to be used in determining color is as follows, except where Trading Rules specify the yellow and/or red to be used in determining given grades:

Cottonseed, peanut, and corn oils	10 yellow to 1 red up to 3.5 red. 35 yellow for 3.5 red or above.
Coconut and palm kernel oils	6 yellow to 1 red up to 3.9 red. 10 yellow to 1 red for 3.9 red or above.
Soybean oil	10 yellow to 1 red up to 3.5 red. 70 yellow for 3.5 red or above.
Tallows, greases, fatty acids, etc.	10 yellow to 1 red up to 3.5 red. 35 yellow for 3.5 to 5.0 red, incl. 70 yellow for above 5.0 red.

C. Notes:

1. Off-color (hue) oils. Some oils, especially soybean, are at times subject to abnormalities in the composition of their pigment content. This results in the occurrence of

hues which cannot be even approximately matched by using the fixed yellow or yellow-to-red ratio designated above. In such cases, if a standard combination is specified (as, for example, prime), report whether the oil is lighter or darker than the standard. If a standard combination is not specified, report the yellow and red glasses which most nearly match the color of the sample.

2. Dark oils. If the color of the oil or fat sample exceeds 40.0 red when using the regular 133.35 mm. column, fill another tube to the 25.4 mm. mark and read the color under the same conditions as described for the longer column. It is assumed that any color result in which the column height is not designated has been read on a 133.35 mm. column. Only when the color has been read on a 25.4 mm. column is it necessary to specify the length of column.

3. The Stevenson colorimeter, Procter & Gamble Co., "Oil and Soap", 13, 18-20 (1936).

2. Petroleum Oils.

The following descriptions of apparatus and instructions are through the courtesy of the Filtrol Corporation:

Laboratory Testing:

It is vital to the refiner who uses a bleaching adsorbent that the latter not only is high in quality but that each lot he receives has the same quality as the previous lot. In the activation of Filtrol adsorbents, advantage is taken of the ability to regulate decolorizing power and other adsorbent properties. As has been described elsewhere, it is possible to regulate these characteristics within narrow limits and at will. The control of quality therefrom becomes important, but it is also quite involved.

The Filtrol Corporation maintains a staff of experienced chemists whose duty it is to see that each lot of adsorbent meets certain rigid product specifications. This requires tests on the adsorbent at progressive stages of its manufacture as well as tests on the finished material. Tests applied to Filtrol adsorbents to assure conformance with product specifications are:

Decolorizing power
Volatile matter

Particle size
Acidity

A brief description of each of these will be given here. If the details of the methods are desired, they can be obtained by writing

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to the sales manager of Filtrol Corporation, 634 South Spring Street, Los Angeles 14, Calif.

Laboratory Control of Filtrol Adsorbent Manufacture:

Decolorizing power. - The decolorizing power of the adsorbent is gaged by determining the color produced when various quantities of adsorbent are added to a given oil, the mixture being properly agitated under given conditions of time, temperature, and speed. Following this contact period, the adsorbent is filtered from the oil. Knowing the amount of a standard adsorbent required to produce equivalent colors on the finished oil, the relative decolorizing power of the adsorbent being tested can then be determined and is usually expressed as percent of the standard.

Volatile matter. - The percentage loss in weight of a given sample of adsorbent after ignition at 1,700° F. for 20 minutes is taken as the percent volatile matter of the adsorbent. Free moisture and water of hydration constitute essentially all of the volatile matter.

Particle size. - The percentage of adsorbent passing through a given standard measuring screen, which is vibrated on the conventional Ro-Tap, is taken as the mesh value for that particular screen. Usually, 200 and 325 are the particle sizes used.

Acidity. - The acidity of the adsorbent is expressed as the weight of potassium hydroxide in milligrams required to neutralize a gram of adsorbent, phenolphthalein being used as indicator. Titration is made on an extract obtained by boiling the adsorbent with distilled water, from which it is subsequently removed by filtration.

Laboratory testing by the oil refiner. - The following test method may be used for obtaining an accurate evaluation of the conditions necessary for securing maximum efficiency in the application of the contact process.

Apparatus for closed unit contacting

1. Contactor.

2. Filtering apparatus.

3. Color machine: The type of instrument preferred for measuring color depends largely on the nature of the work, i.e., plant control, research, etc. Greatest accuracy is obtained by optical-density color methods; hence, these will serve best for technical studies of a research nature. For routine plant control it is satisfactory to use a commercial color test, of which the Tag-Robinson

and Lovibond methods are to be preferred, as these in some measures express color density. The N.P.A. color accuracy may be increased to a marked degree by the adoption of one-quarter shade chemical standards to supplement the usual full and half number A.S.T.M. color glasses. The apparatus as pictured consists of an iron or stainless-steel pot of about 300 ml. capacity, which, during the test, is attached to a fixed head in the contactor assembly. Also attached to the fixed head are a steam inlet tube, mechanical stirrer, and a metal, water-cooled condenser. (See fig. 4.)

Procedure:

1. Weigh 300 grams of the oil to be bleached into the contactor pot.

2. Add weighed portion of the adsorbent corresponding to the desired adsorbent dosage to the oil.

3. Assemble apparatus.

4. Contacting cycle to be as follows:

Preliminary: Blow superheated steam line free of condensed water. When contactor pot with the oil-adsorbent mixture is screwed in place, the stirrer is adjusted to give uniform agitation at a moderate rate throughout the entire cycle. Note time when heat is applied.

Zero time: Heat is applied at a uniform rate. The burner adjustment is not changed until maximum temperature is reached. The average rate of temperature rise is approximately 50° F. per minute.

3 minutes at 300° F.: The superheated steam is admitted and adjusted to give a condensed steam overhead of approximately 1 ml. per minute. The volume at the end of the contact period should be between 15 and 20 ml.

10 minutes at 550° F.:* The average time to reach maximum temperature is 10 minutes; allowing for a 10° lag, burner should be adjusted at 540° F. Temperature is maintained at 550° ± 2 for 10 minutes, ± 15 seconds.

15 minutes at 550° F.:* Flame extinguished and door of flame guard opened.

22 minutes (approximately) at 440° F.: Turn out superheated steam from oil-adsorbent mixture.

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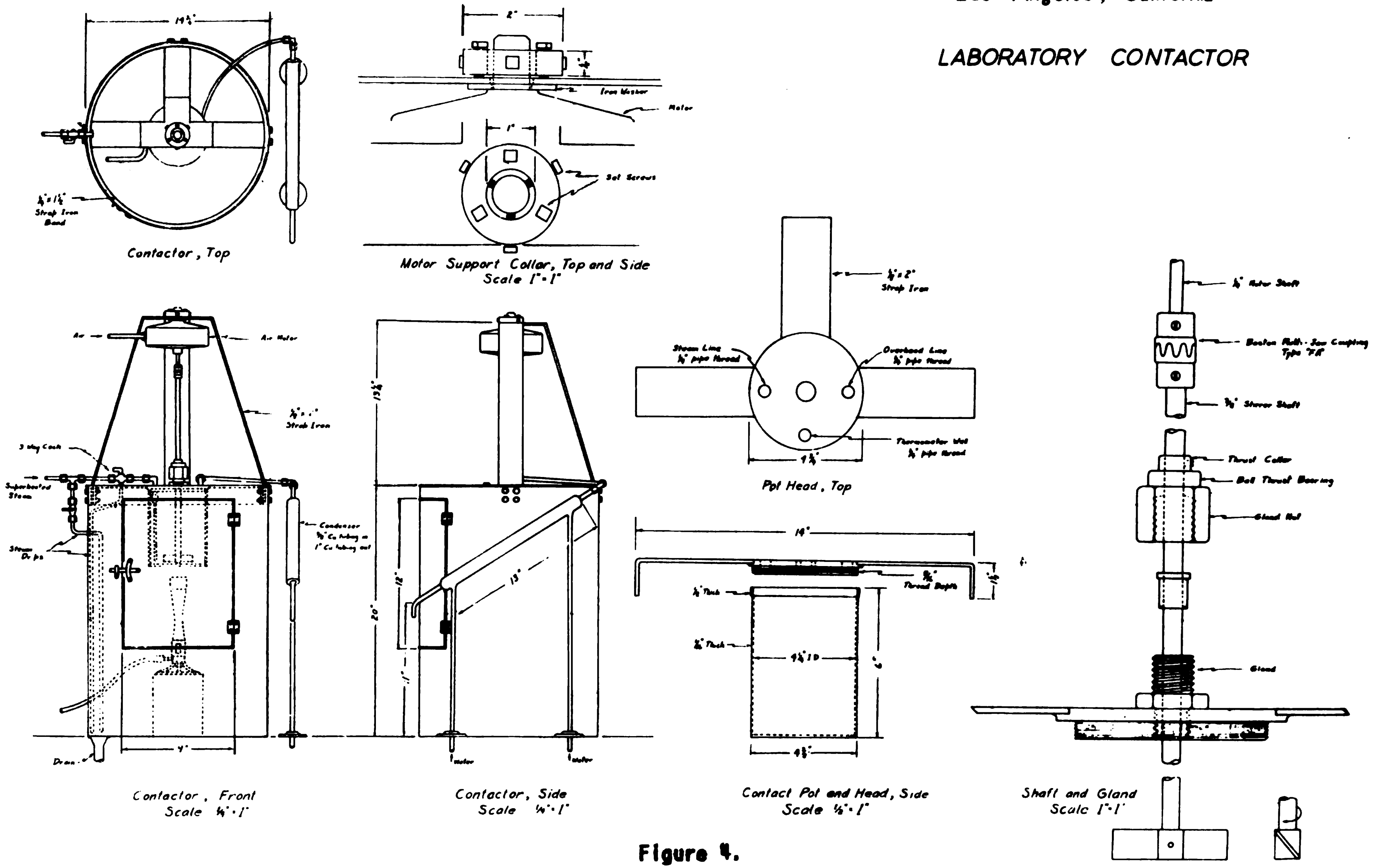
*Bright stock type oils, contact temperature approximately 550° F. Neutral stock type oils, contact temperature approximately 320° F., filter temperature 250° F.

Los Angeles, California

LABORATORY CONTACTOR



Contactor, Top

Motor Support Collar, Top and Side
Scale 1" = 1"

Pot Head, Top

Contactor, Front
Scale ¼" = 1"

Contactor, Side
Scale ¼" = 1"

Contact Pot and Head, Side
Scale ½" = 1"

Shaft and Gland
Scale 1" = 1"

Figure 4.

25 minutes (approximately) at 350° F.: Stop stirrer, remove contactor pot from assembled apparatus, and filter contacted oil immediately through a suction funnel.

5. Color determination:

After filtering, the finished oil is placed in a 4-oz. sample bottle, stoppered, and allowed to cool to room temperature. Color of the finished oil is determined.

Optimum contacting temperature: A series of contacts using a fixed adsorbent dosage and varying the top contacting temperature may be made. These contacts should be evaluated on the basis of color removal and overhead loss (if excessive at higher temperatures).

Optimum contact time: Select the temperature from the previous series that gave the best results and, using this temperature and a fixed adsorbent dosage, vary the contact time. Using the same standards as before, the optimum contact time may be selected.

When the optimum contact conditions of time and temperature have been determined, a series of contacts may be made by varying the clay dosage in order to determine the proper amount of adsorbent to use in order to reach desired color level.

3. Vegetable and Mineral Oils.

The following methods and apparatus were developed by the Bureau of Mines for evaluation of clays. They were developed from the standpoint of the clay laboratory rather than for industrial work. The primary interest here is the relative merits of clays for the general purpose of bleaching. There is no particular need for the high accuracy employed in industrial control.

A. The first method gives an evaluation on both bleaching efficiency and oil retention and is particularly good with vegetable oils but lacks accuracy with petroleum oils, as the mixture of oil and clay is exposed to air during the stirring, and the mineral oil tends to darken.[5]

1. Bleach test. 300 grams of oil are weighed into a mixing cup, heated to 120° C., and 6 percent of official fuller's earth (A.O.C.S.) is added. The mixture is stirred mechanically at 250 r.p.m. ± 10 for 5 minutes, not allowing the temperature to fall below 105° C., and is filtered through paper. The oil is then given a color rating in a colorimeter.

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[5] Good, William W., Study of Control Tests in the Contact Process of Decolorizing Edible Oils: Unpublished thesis submitted for master's degree, University of Alabama. Work done under supervision of Dr. S. J. Broderick, Bureau of Mines, 1941.

2. Oil retention. If an oil-retention evaluation is desired, the following procedure is employed: The oil is decolorized as above, and at the end of the agitation period the clay-oil mixture is transferred to a Seitz filter, as shown in figure 5. Whatman No. 1 filter paper is used. Suction is then applied by a Cenco-Megavac pump or similar apparatus. The Seitz filter is enclosed by a heater, also shown in figure 5.

The heater is so regulated by a rheostat that the cake temperature is maintained at 70° C., measured by a thermometer with bulb resting on top of the filter cake. By filtering at the constant temperature, runs do not vary more than 0.5 percent on oil retention. A fixed time of 2 hours for the filtering will be found satisfactory, the recording of the time beginning after the free oil passes through the filter cake.

The filter cake is then removed and weighed. The weight of the original clay subtracted from the weight of the cake gives the weight of oil retained. The weight of the oil retained multiplied by 100 and divided by the weight of the cake gives the percentage of oil retention in the cake.

A Buechner filter might be used but is unsatisfactory, as compared to the Seitz, as the filter paper cannot be clamped down and the ratio of the area of the opening in the bottom is small compared to that in the Seitz filter.

Temperatures above 70° C. are likely to result in cracking of the filter cake, with subsequent decrease of the vacuum and consequent erratic results. Moreover, with temperatures in excess of 70° C., spontaneous combustion may occur with some clays when using vegetable oils.

The matter of spontaneous combustion is important commercially when clarifying vegetable oils. In the industrial processing, the filter cakes are "blown out" with air after filtering. Some of the oil-impregnated fuller's earths (notably those of the Alum Bluff formation in Georgia and Florida) will catch fire under these conditions. To determine clays of this nature it is only necessary to modify the laboratory procedure given above by holding the filter cake at 100° C. instead of 70° C. If combustion does not take place in the 2-hour interval of filtering, the clay does not have the characteristic of causing spontaneous combustion. Those that do, usually fire in about three-quarters to one hour.

B. The second method is one for decolorizing. No special apparatus is required, and the test may be made with a minimum of time and observation[6]. It has been found to be unusually good for work in the clay laboratory, and comparisons with the hot-contact method indicate that it may be useful for plant-control purposes.

Essentially, the method consists in mixing the sample of clay with a standard oil, shaking in an Erhlenmeyer flask, filtering, and testing the oil

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[6] Ross, D. W., Identification and Evaluation of Bleaching Clays: Bureau of Mines Rept. of Investigations 4295, 1948, 26 pp.

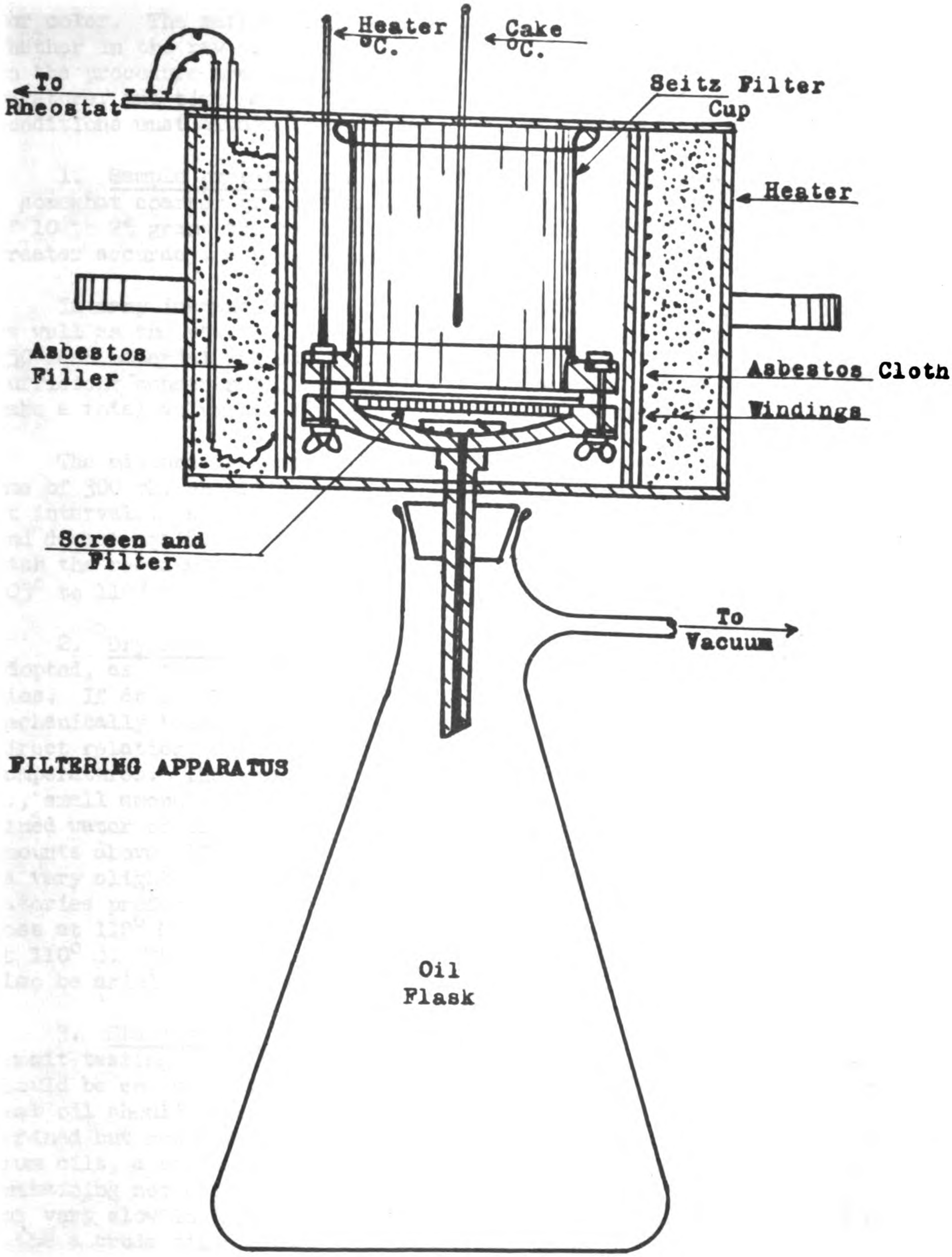

Figure 5. - Seitz filter.

for color. The method applies equally well to any oil stock and to any clay, whether in the raw or activated states. Although the various individual steps in the procedure are not critical, in that other sizings of the sample, temperature, and time may be different from the recommended procedure, uniform conditions must always be employed. The recommended procedure is as follows:

1. Sample preparation. The material is ground through 150-mesh screen. A somewhat coarser grind does less bleaching, and a finer grind more. Samples of 10 to 25 grams are handled conveniently in a 250-ml. flask. However, for greater accuracy, a 50-gram sample may be employed, using a larger flask.

In many instances it is desired to test the clay in the activated state as well as the raw. To activate the clay, take a 50-gram sample of the dry 150-mesh material and add it to 200 ml. of distilled water. Then add slowly sufficient concentrated sulfuric acid (95 percent H_2SO_4, gravity 1.84) to make a total volume of 300 ml. This is conveniently done in a 600-ml. beaker.

The mixture is then brought to a boil and kept boiling 1 hour. The volume of 300 ml. should be kept approximately constant by adding distilled water at intervals. At the end of an hour, decant while hot. Refill with water and decant again, and repeat 4 to 5 times. Then pour through a filter and wash the residue half a dozen times. Dry the residue to constant weight at 105° to 110° C. and proceed with the decolorizing test as outlined above.

2. Drying of sample. The drying temperature of 105° to 110° C. was adopted, as it is a temperature used almost universally in chemical laboratories. If dried to constant weight at this temperature, all but traces of mechanically held moisture are driven off. Moisture in a sample has a very direct relation to decolorizing, particularly in laboratory testing at room temperatures. The more moisture, the less the bleaching power. Above 110° C., small amounts of moisture exist up to the point where the chemically combined water of the clay is given off, 450° to 600° C. Even these small amounts above 110° C. have a noticeable effect upon the decolorizing, but it is very slight, compared to the moisture retained below 110° C. Many laboratories prefer to dry at 150° to 160° C. to constant weight, as the equivalent loss at 110° C. may be obtained in a few hours, as compared to about 5 days at 110° C. The standard clay or official sample employed for reference should also be dried at the same temperature adopted for the sample.

3. Standard oil stock. A sufficient amount of stock should be kept to permit testing a large number of samples. When a new supply is obtained it should be checked for color and viscosity against the old stock. A gallon of test oil should be sufficient for 100 to 200 tests. For vegetable oils, a refined but not clarified cottonseed oil serves as a good stock. For petroleum oils, a refined but unclarified stock of comparatively low viscosity containing not over 0.5 percent sulfur is satisfactory. High-viscosity stocks are very slow in filtering. However, the most satisfactory stock will be found to be a crude oil of low viscosity, such as Kettleman crude from California (neutral, sp. gr. 40.3° Be). This was used in developing the present test. Dr. P. G. Nutting employed this stock in running tests on several thousand

clays for the Federal Geological Survey.[7] Because of the dark color of the crude oils, it is necessary to dilute with water white gasoline, naptha, or benzol. With the Kettleman crude, the proportion of about 4 ml. per gram of clay will be found satisfactory. The amount of oil concentration will be varied from 0.1 ml. to 1.0 ml. per gram of clay.

To determine whether or not a clay is of the bleaching type, an oil concentration of 0.2 ml. per gram of clay is useful. If the clay is a bleacher, then several increasing concentrations should be tried in order to determine the full bleaching range of the clay. Many clays have short ranges and would not be suitable for commercial usage.

Several concentrations may be added to separate portions of a clay sample, and all treated at the same time; or one may start a single sample at the lowest concentration and, after decolorizing, filtering, and testing for color, pour the oil and clay residue back into the flask with the next higher oil concentration and repeat the process. The latter method is, of course, time-consuming.

4. Mixing. The clay-oil-benzol mixture is placed in an Ehrlenmeyer flask, the flask stoppered and placed in a laboratory mechanical shaker, and shaken for an hour. If a mechanical shaker is not available, then the equivalent agitation may be obtained by vigorously hand-shaking the flask or flasks every 10 minutes for a period of 2 hours. Less time than the above will cause a very appreciable lowering of the decolorizing effect and less accuracy in duplicating results. More time than this has very little effect.

5. Filtering. Ordinary glass funnels are used with a filter paper suitable for fine-grained to medium precipitation. Buechner funnels may be used; but with low-viscosity stocks, the ordinary funnels filter in reasonably short time.

6. Color test. The filtered oil is now ready for the color test. Any colorimeter that has been accepted as standard by the oil industry may be used, or one may set up a standard of one's own. The color tests and colorimeters will be discussed more fully below.

Percolation Methods

1. Industrial Method

The following equipment and procedure are used by the Attapulgus Company[8]

> It should be observed at the outset that problems involving laboratory percolation filtration fall, generally speaking, within two broad classes, differing chiefly in the matter of the scale upon which the tests are conducted. These classifications may be described as follows:

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[7] Nutting, P. G., Adsorbent Clays, Their Distribution, Properties, Production, and Uses: Geol. Survey Bull. 928-C, 1943, pp. 127-221.

[8] Research and Development Department, Attapulgus Clay Co., Absorbent Testing and Its Application to Refining Problems: 1940, 12 pp.

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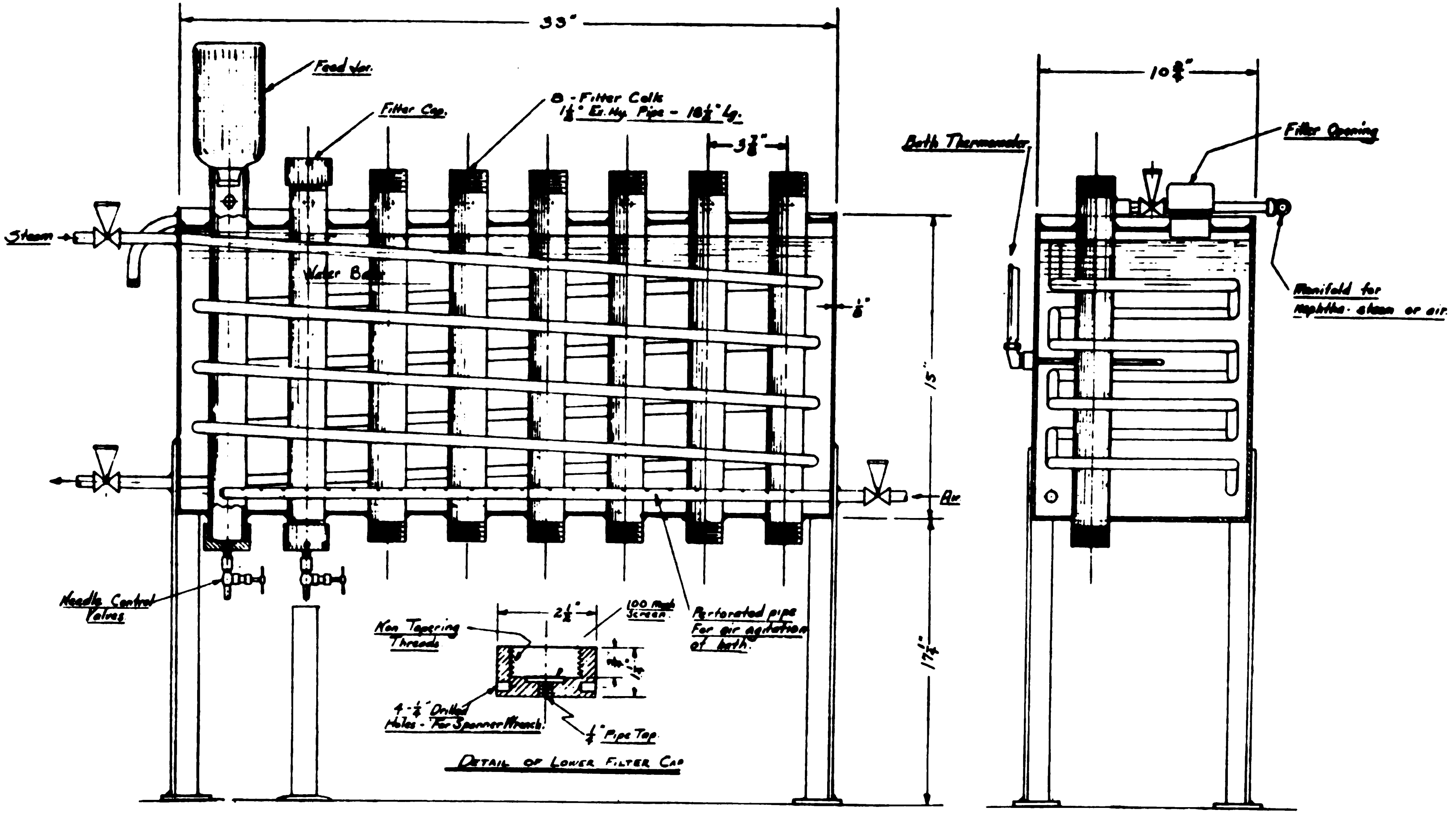
33"
Feed Jar.
Filter Cap.
8 - Filter Cells
1½" Ex.Hy. Pipe - 18½" Lg.
3⅞"
Steam
Water Bath
⅛"
15"
Air
17¼"
Needle Control
Valves
Non Tapering
Threads
2½"
100 Mesh
Screen.
Perforated pipe
For air agitation
of bath.
4 - ¼" Drilled
Holes - For Spanner Wrench.
¼" Pipe Tap.
DETAIL OF LOWER FILTER CAP
10⅜"
Bath Thermometer
Filter Opening
Manifold for
naphtha - steam or air.

Figure 6.

(1) Comparative efficiency and filterability tests, in which the problem is essentially one of obtaining comparative yield or efficiency data without the necessity of correlating laboratory and plant results, and,

(2) Processing tests, in which are involved the correlation of plant and laboratory yields, the production of oil for inspection or subsequent processing, or the study of adsorbent regeneration.

As previously stated, the problems to which these techniques may be applied differ primarily in the scale on which the tests are run, and it is proposed * * * to discuss each in turn, and to point out some of the uses to which they * * * may be utilized to advantage by the refinery laboratory.

A. Description of Laboratory Percolation Techniques

(1) Comparative Efficiency and Filterability Tests

The apparatus recommended for use in tests of this nature is shown. (See fig. 6.) It consists of a series of eight filters 1-1/2 inches in diameter and 18-1/2 inches long inserted in a water bath heated by steam. Each filter is equipped with a brass cap containing a needle valve for close adjustment of the rate of percolation, whereas a section of 100-mesh screen welded into the cap acts as a support for the adsorbent. The filters should be mounted on a table at least 37 inches high, and should be placed in a position affording good illumination for both day and night work.

Auxiliary equipment includes a tamping rod; A.S.T.M. color comparator and color standards (1/4 shade intervals); 50 and 250 cc. graduated cylinders; balance sensitive to 1/8 gram; interval timer; and the requisite feed and composite bottles. A graduated metal container in which the adsorbent may be weighed also has been found to be helpful. * * *.

The following procedure is followed in conducting percolations. Strict adherence to details is essential to the obtaining of the high degree of precision which the method affords.

1. Adjust the bath to the required temperature. The temperature should be maintained at plus or minus 1° throughout the test.

2. Thoroughly clean the filter tubes, valves, and glassware, and assemble filters. Open valves halfway. Fill the charging bottles (32 oz.) with the charging solution or oil, cork, and place in a convenient location.

3. Assemble the adsorbent samples to be tested, and prepare the filtration data cards, entering all required data in ink.

4. Tare the weighing container and accurately weigh the amount of adsorbent that will give a column height of 16-3/4. (As all filters are run on equal volumes, it will be found convenient to mark the container with a graduation designating the level reached by the standard volume. For No. 1 fuller's earth, the amount required is approximately 200 grams; for bauxites, about 375 grams.)

5. Place one-third of the adsorbent in a funnel, the outlet of which is corked. Remove the stopper and permit the material to flow into the filter tube. Insert the tamping rod and allow it to drop freely into the filter tube three times, guiding it lightly with the fingers. (Tamping is a vital part of the percolation test, and the technique should be carefully standardized.) Add another one-third portion of the adsorbent and repeat the tamping. The final portion is charged to the filter in the same manner. When charging is completed, measure and record the outage in each tube.

6. Invert the charge bottles over the filters, allowing them to rest on top of the tubes. Record the time of starting and the time at which the filters show through. The filters should all show through at about the same time, and any filter that manifests a too-wide variation should be discarded. Solution filters should be shut in for 3 minutes after showing through and then be restarted, the rate being adjusted in accordance with * * *. (Fig. 7.)

7. Collect the filtrate in 250 cc. cuts. As one graduate becomes filled, move another in its place and empty the first into the composite bottle after recording the exact volume and temperature of the fraction and the time at which it was taken. Return the empty graduate to its place on the filter table ready for use under the same filter.

8. Shake the composite bottles thoroughly and pour a 50 cc. sample into the color test glass. Place the color test glass in the comparator and determine the ASTM color. After the color has been recorded, return the sample to the proper composite bottle.

9. When the composite color approaches 4 ASTM., replace the 250 cc. graduates with cylinders of 50 cc. capacity and reduce the volume of the cuts to 50 cc. As the composite color nears 5, reduce the fractions to 5 cc., thoroughly mixing the composite after each cut is added and before the sample for color determination is withdrawn. (If the yield is to be determined at some color darker than 5, the reduction in volume of the fractions is, of course, made when the composite color is one shade lighter than the finished color desired.)

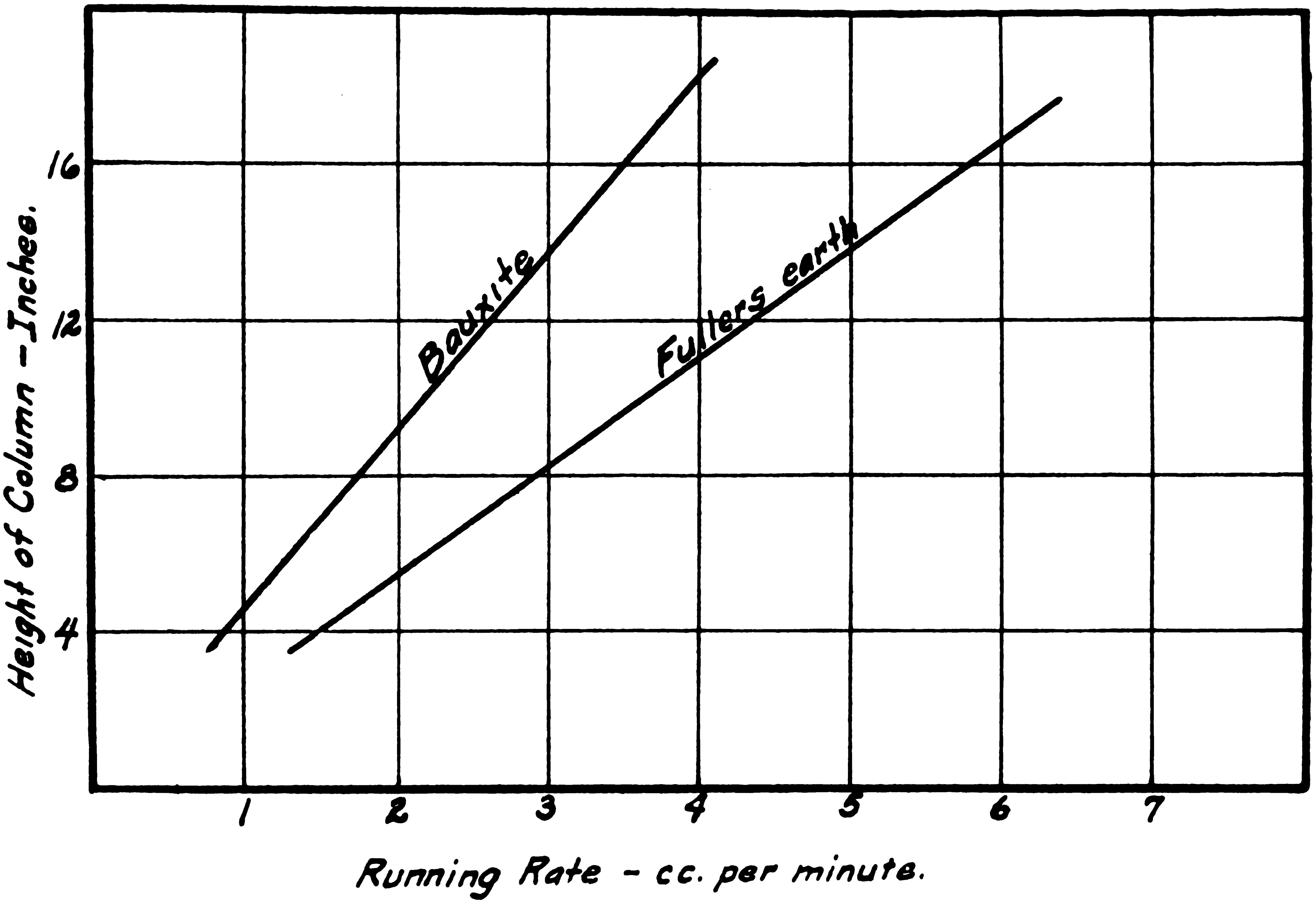
Height of Column - Inches.
16
12
8
4
Bauxite
Fullers earth
1
2
3
4
5
6
7
Running Rate - cc. per minute.

Figure 7.

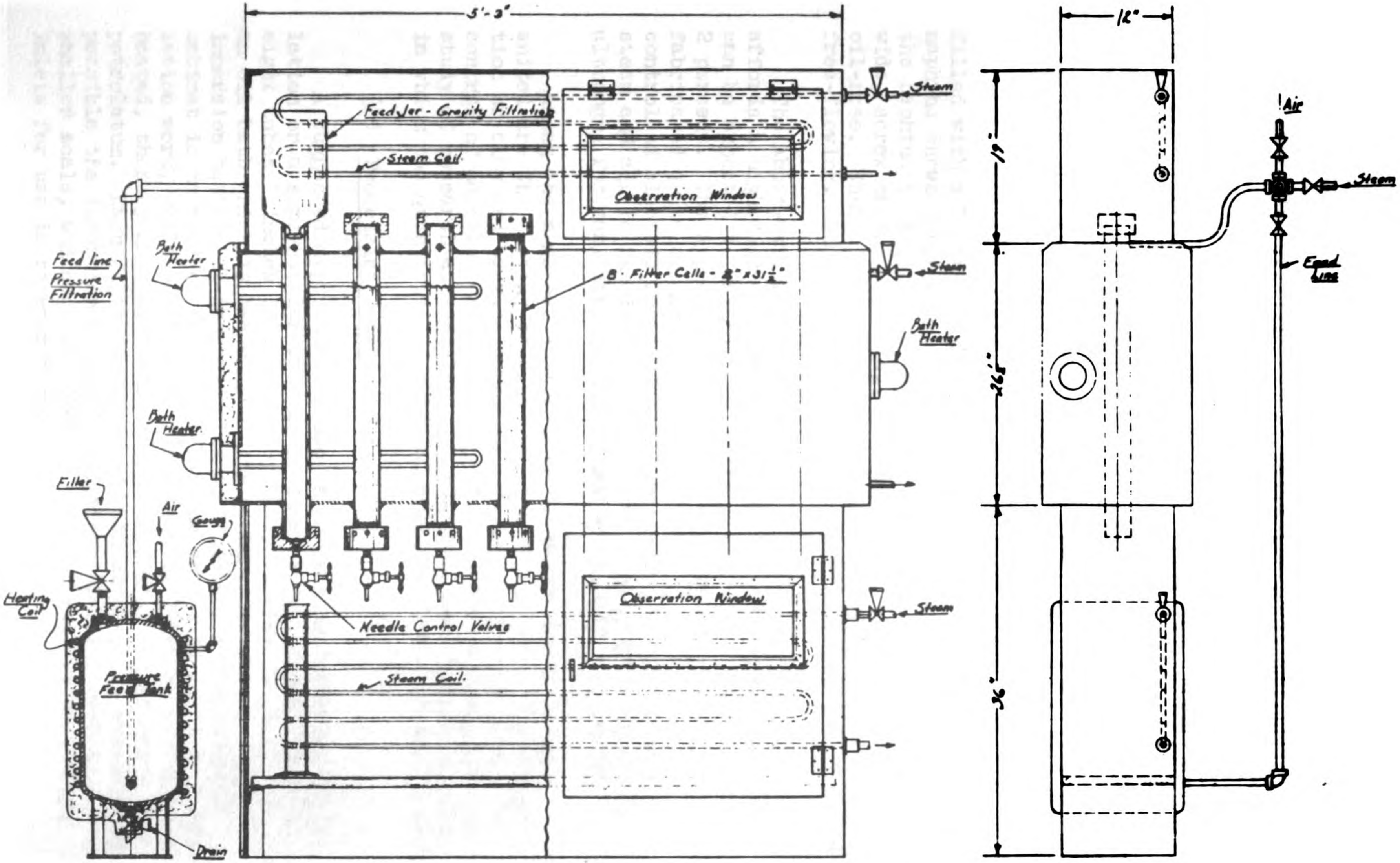

Figure 8. - Apparatus for use in conducting laboratory percolation.

10. From the total yield to 5 color and the weight of adsorbent charged, calculate the yield as barrels per ton (cc./gram x 5.71). Calculate also the yield in barrels per thousand cubic feet (bbls./ton x $\frac{\text{volume weight}}{2}$), and enter the yield data on the filter card. If yields at other colors are desired, prepare a plot of yield vs. composite color from the filter card data, and read the yields at the desired color from the curve. (Yields obtained in this manner are not to be regarded as possessing the same accuracy as those experimentally determined at the final color.)

11. When the filtration is completed, remove the feed bottle and allow the filter to drain. When most of the oil has run out, the filter may be dumped. If the adsorbent is to be revivified, allow the filter to drain thoroughly, and invert a 1-pint bottle filled with solvent naphtha in the top of the tube. When the naphtha shows through allow to soak for 20 minutes and then permit the naphtha to drain from the column. Next, open the bottom valve wide, screw on the top caps, and steam until the escaping vapor is oil-free. Shut off the steam and blast with air until the clay is free-flowing. Dump the filter and package and label the adsorbent.

The above-outlined test, with rigid adherence to details, affords a high degree of precision, and an experienced operator can be expected to maintain an accuracy of within plus or minus 2 percent. The apparatus is of convenient design and may be fabricated quite economically. (See fig. 6.) The provision of controlled electric heating and of manifolds for the supply of steam and air to the individual filters is greatly to be desired, although, for many applications, they may be dispensed with.

Among the numerous applications to which the procedure is suited are the testing of clay and bauxite receipts; the evaluation of clay and bauxite samples of various burning numbers; the control of adsorbent regeneration and of filter washing; and the study of research and development problems involving percolation in which the quantities of material available for test are limited.

(2) Processing Tests

A suggested apparatus for use in conducting laboratory percolation on a somewhat larger sale is shown (fig. 8) and comprises eight tubes 2 inches in diameter by 31-1/2 inches in height set in an oil bath which is heated, both by steam coils and by electric immersion heaters thermostatically controlled. A steam-heated cabinet is mounted on top of the bath as an aid in straight percolation work, while the bottom of the bank is likewise enclosed and heated, thereby greatly facilitating the filtration of waxes and petrolatum. Each filter is equipped with an adapter, which makes possible the insertion of smaller-dimater tubes for work on a smaller scale, and each is likewise provided with steam and air inlets for use in regeneration.

The filter caps and other accessories are essentially similar to those previously described. Another feature, however, is the pressure tank at the left of the bank, which is connected to the tubes by means of the steam manifold and which makes it possible to operate the filters under pressure through the use of a cylinder of inert gas.

The procedure employed in conducting percolation tests on this scale is, in most respects, comparable to that which has been outlined above. The filters are charged to a height of 25-3/4 inches, requiring approximately 570 grams of No. 1 fuller's earth or 1,050 grams of bauxite. After showing through, the filters are shut in for 20 minutes and are then permitted to flow at a rate of 15 cc/-minute for fuller's earth and 8 cc/minute for bauxite. In the event of a reduced column height, as is encountered, for example, in running revivification series, the rate is adjusted in accordance with the curves in (fig. 9), which shows the rates that are imposed in the percolation of materials other than cylinder stock solutions.

The utilization of this type of apparatus is desirable in connection with problems in which the correlation of laboratory and plant results is of importance. It is also, of course, suited to problems in which the production of considerable finished oil is a requisite, as in the solution percolation of a stock for subsequent reduction and straight finishing. Its utility in research and development work, involving study of high temperatures and pressures, is also obvious.

While the correlation of plant and laboratory filter yields is admittedly a problem for the individual refinery, owing to the variation in equipment, operating conditions, stocks, etc., it has, nevertheless, been possible, through the use of this technique, to achieve what is felt to be a highly satisfactory degree of correlation.

It may be stated that all of the percolation problems with which the refinery laboratory is likely to be confronted may be resolved through the use of one or the other of the foregoing techniques. Nearly all of such problems, however, call, in addition to filtration data, for determination of certain physical characteristics of the adsorbents undergoing test. These include determinations on grain size, volume weight, volatile matter, and abrasion characteristics.

B. Application of Adsorbent Testing Techniques to Refinery Problems

(1). Evaluation of Adsorbent Receipts

It is a duty of nearly every laboratory to maintain a check upon the quality of shipments of adsorbent materials received at the refinery and to compare the characteristics of competitive products or of different types of filtering media. The smaller-scale procedure that has been discussed is admirably suited to

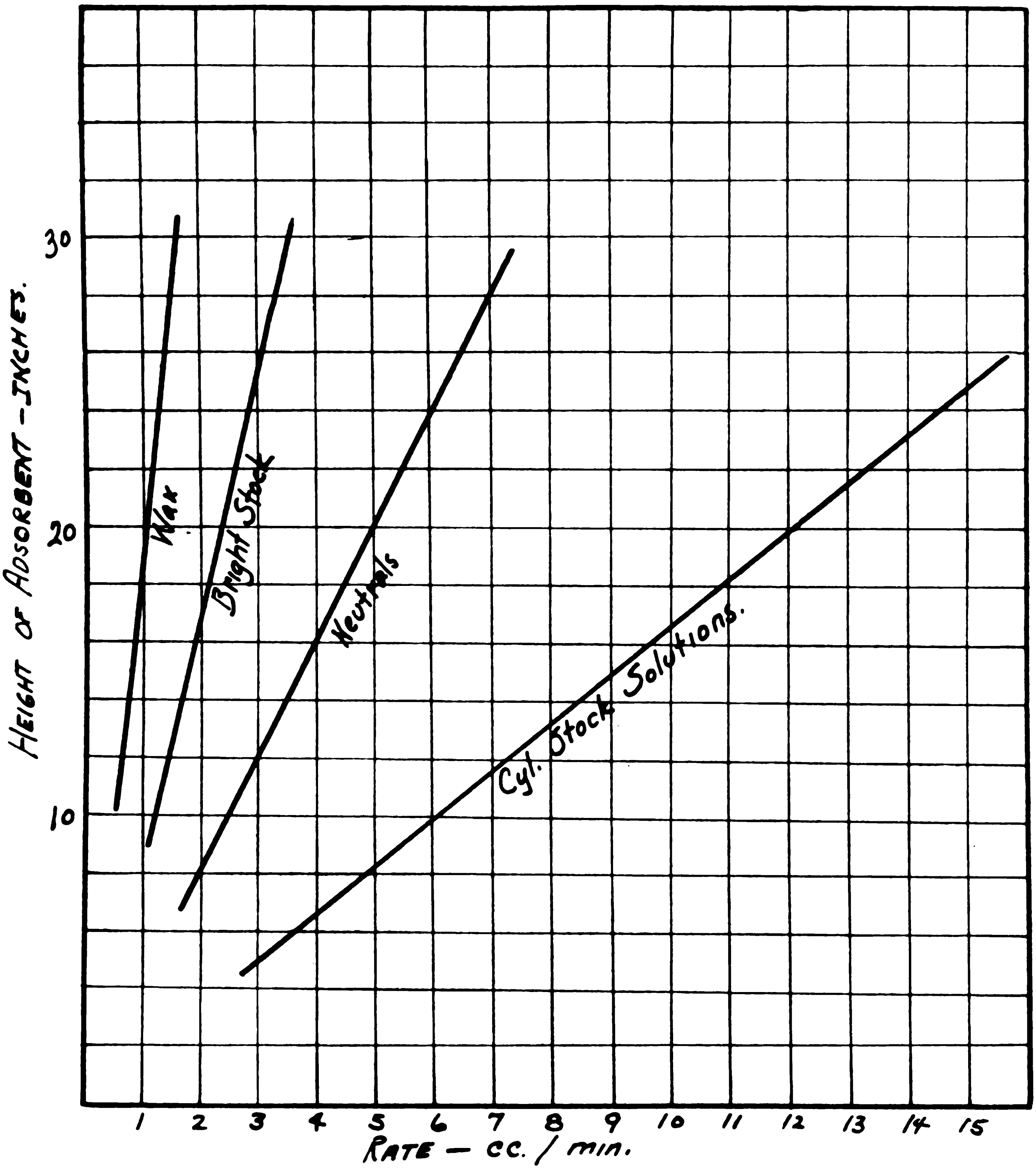
30
20
10
Height of Adsorbent - Inches.
Wax
Bright Stock
Neutrals
Cyl. Stock Solutions.
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Rate — cc. / min.

Figure 9.

this type of problem, and it is proposed here merely to point out certain precautions that have been found essential to accurate testing and to enumerate the data that should be obtained.

A prime requisite in attacking problems of this nature is the selection and adoption of a reference standard to which the values of all samples tested may be related in terms of percent efficiency. This standard material, fullers earth or bauxite, as the case may be, should be absolutely uniform, and a sufficient quantity should be obtained and mixed to serve the needs of the laboratory for several years. It should, preferably, be material as received at the refinery, although many laboratories will find it more convenient to utilize a sample from the first plant burning of the adsorbent.

A sample of the reference standard material should be run with every set of filtrations, instead of using it for the standardization of a quantity of test stock and referring yields obtained on test samples run subsequently to the standard yield obtained, perhaps, some weeks earlier. Experience has taught that the inclusion of a filter of the reference standard in every set run is the only certain method of obviating the inevitable inaccuracies that are introduced by slight deviations in charge stock, column height, etc.

The column height of the standard filter should always be identical with that of the sample undergoing test. If new material is employed as the standard, it should first be burned in accordance with the recommended procedure. If, on the other hand, the standard is a plant-burned No. 1 sample, it suffices to bring it to a temperature of 400° F., maintaining it at this temperature for 30 minutes. No deviation from this requirement of preliminary drying is permissible.

Given a satisfactory reference standard, the testing of adsorbent receipts and of miscellaneous samples resolves itself into careful sampling of the batch to be tested; preliminary burning by the standard procedure; screening to remove fines produced in the burning; and determination of the percolation efficiency in terms of the standard. In all comparisons of this nature, the mesh size of the samples being compared should be substantially identical, and it is important that artificially produced fines be removed prior to testing.

For most of these routine evaluations a 60/40 solution of cylinder stock in solvent naphtha is recommended as the test stock. Clay samples should be compared at filtration temperatures of 135° F., bauxite samples at 180° F. The use of the lower filter rates shown in (fig. 7) is essential to the satisfactory testing of new bauxite samples, as, otherwise, the early "break" in the cast of the filtrate will render the accurate reading of the final color extremely difficult.

In addition to percolation efficiency, adsorbent receipts should be tested for volatile matter, mesh size, volume weight after calcining, and resistance to abrasion.

(2) Control of Fuller's Earth Burning

The control of fuller's earth burning through examination, at frequent intervals, of samples of earth of various burn numbers is likewise an important function of the refinery laboratory, in connection with which the material presented in this discussion is of decided pertinency. As a matter of routine, it is recommended that monthly composite samples be collected representing all of the burning numbers through which clay is used, and that all of the samples be tested for volatile matter, volume weight, and mesh size, as well as for percolation efficiency on cylinder stock solution, using the small-scale technique. In the event that certain of the earlier numbered clays are employed in the plant for neutral filtration, the composite samples representing those numbers should likewise be tested, using a neutral stock, as by this means data may be obtained that would result in recommendations directed toward a more economical distribution of the decolorization load.

In the testing of series of samples of this type, it is important that the samples be dried at 400° F. prior to evaluation and the determination of the physical inspections. Rescreening before charging to the filters is not desirable, as deviation in particle size is a normal characteristic of series of this nature. Finally, it should be borne in mind that the apparent density of fuller's earth increases materially upon continued regeneration, so that, in interpreting and reporting results, emphasis should be placed upon the volume basis efficiencies.

The data resulting from the study should be plotted and compared with results from previous analysis of a similar nature. In the event that indications point toward a degradation in average efficiencies, analysis of the physical tests and of operating conditions will point the way toward correction of the difficulty, as analysis of volatile matter and volume weight tests coupled with values for the viscosity oil content of the spent clays enables the laboratory to reach a conclusion as to whether the reduced efficiencies are traceable to overburning, underburning, etc.

At intervals of at least every 6 months, a cost analysis should be made for the purpose of determining whether, under existing operating conditions, the fuller's earth is being discarded at the optimum point. This analysis should also be carried out on any occasion of drastic readjustments in filter house throughput, and should, of course, include consideration of the distribution of the various services between early and late number clays.

(3) Control of Bauxite Burning

The testing problems incidental to the control of bauxite burning are essentially comparable to those already discussed in connection with fuller's earth although simplified by the fact that there are seldom more than two grades to be tested, as compared with the 15 or 20 fuller's earth burn numbers that must be checked. It is therefore possible to maintain a closer check on operations, and it is accordingly recommended that representative samples of the filter-house charge be evaluated at bi-weekly intervals.

These samples should, after drying at 400° F., be evaluated in comparison with the reference standard, on the major stocks for which the material is used in the plant. Determination should also be made of volatile matter, mesh size, and volume weight, in addition to which it will frequently be found helpful to apply the test for determination of nonbauxitic contamination.

In the event that batches of bauxite are, as is frequently the case, segregated and specially handled for use in the filtration of such materials as neutrals, waxes, and petrolatum, it is of particular importance that frequent checks upon filter yields be effected, as departure from the prescribed conditions of operation may result in serious losses in yield. In these evaluations, and, in fact, in all efficiency tests on bauxite samples, it is desirable to determine yields at various colors and to report the results in the form of color vs. yield curves.

(4) Control of Filter Washing

A further instance of an important application of the laboratory percolation test to refinery operation is represented by the part that it can be made to play in the proper control of the filter washing step, inadequate handling of which can result in serious increases in decolorization costs. Ridgeway, Ross, and Henderson (Refinery, November 1938, p. 546) have presented data on the washing of fuller's earth filters, which demonstrates conclusively the depressing effect upon yields which is exerted by the incorporation of small quantities of color bodies washed from the clay in the charge to a subsequent filter.

A fact which renders it of even more importance that the individual plant laboratory be equipped and its personnel trained for the execution of investigations of this character is that conditions of operation and of charging stock vary widely from plant to plant, making it difficult to generalize in this respect. * * *. It is possible, by sampling the wash at five-barrel intervals, reducing, and running small-scale comparative filterability tests, to procure data upon which to base recommendations as to optimum wash volume, and the optimum division between recycle and filter butts.

Since the maintenance of a balance between oil and tar left in the bauxite and the relative quantities recycled to a subsequent filter or reduced as filter butts is of the utmost importance from the standpoint of refining costs, it is recommended that tests such as these be carried out periodically, and that checks be made at any time that the character of the unfiltered stock undergoes a change.

(5) Prediction of Percolation Results and Optimum Operating Conditions

The prediction of filter yields and of finished oil characteristics is an additional problem with which the refinery laboratory is often confronted and to which the techniques presented herein may be applied to advantage. In cases involving totally unfamiliar stocks, or those of a borderline nature, the problem frequently must first be approached from the standpoint of the determination of the optimum conditions of application of the adsorbent to the particular oil in question.

In respect to the latter aspect of the problem, the use of the smaller-scale apparatus is best suited, since the results desired are of either a qualitative or strictly comparative nature. In studies of this type, investigation should be made of the influence of filtration temperature, burning temperature, and percolation rate, particularly where the adsorbent to be utilized is bauxite, which is appreciably more sensitive to variations in filtering conditions than is fuller's earth.

The information thus obtained on a qualitative scale is then utilized in the large filters for the purpose of predicting the results to be anticipated in plant practice. While the wide variations in filter shapes and sizes which exist in the industry make it virtually impossible to generalize with respect to the correlation of yields, it may be stated that experience has shown it to be possible, in a given plant, to arrive at an excellent correlation. Results in this respect are appreciably more satisfactory when the larger filters are used, particularly in the case of bauxite. Correlation with respect to finished oil quality predictions makes the use of the larger apparatus mandatory.

(7) Miscellaneous Applications

Numerous other applications of the percolation procedures exist, including problems relating both to plant control and to research and development. Achievement of the optimum balance between solution and straight percolation in the decolorization of bright stocks is a case in point, as is the analysis of variations in other processing steps, for example, dewaxing, upon results to be expected from the percolation plant. Many other problems of a more specific interest to a given refinery will occur from time to time.

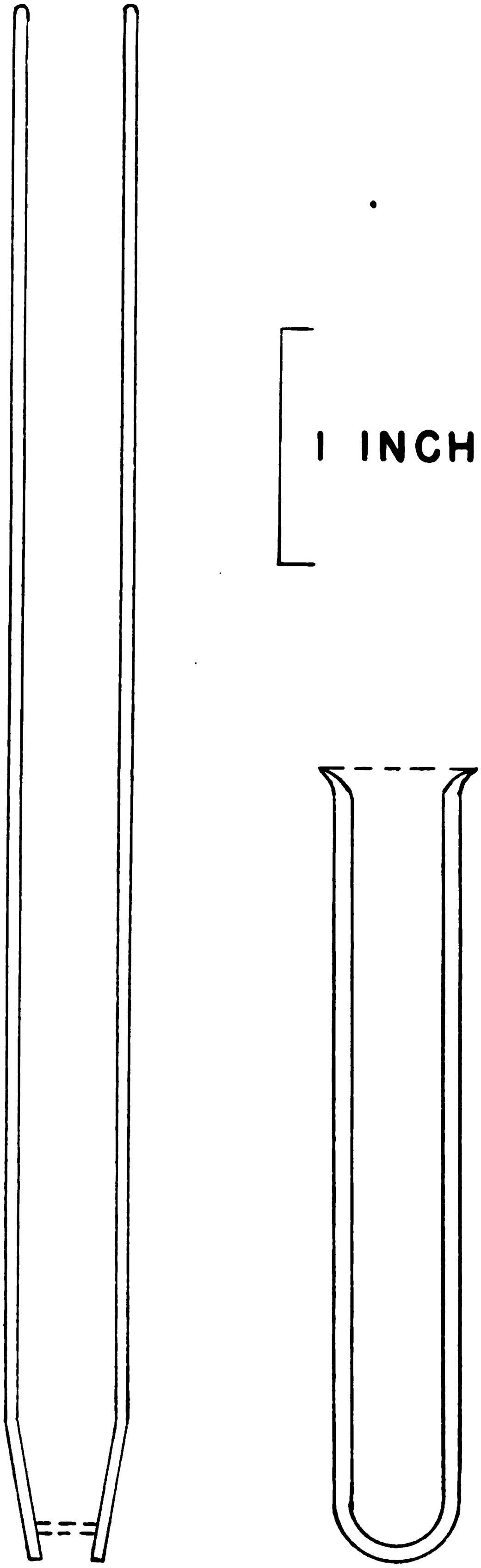

Figure 10.

It is felt that the testing methods presented in this paper represent potentially valuable tools for use in refinery laboratory operations, and that through their application any problems relating to the use of adsorbent materials may be investigated successfully. Finally, it is felt to be highly unfortunate that such wide variations exist between the techniques employed by the different technical groups of the industry, and it is hoped that this contribution will aid in bringing about a greatly to be desired standardization.

2. Federal Geological Survey Method

The following method was used by Dr. P. G. Nutting in evaluating clays[9].

Percolation tests are made on clay ground to pass a 150-mesh (0.1-millimeter) sieve. This is just fine enough to permit action by all the clay and sufficiently coarse to permit the test oil to pass at a reasonable rate. About 3 grams, or a level teaspoonful, of this ground clay is dried for an hour in an oven at 160° C. (320° F.), then put in a porous-bottomed tube to the depth of an inch or more. To avoid channeling, it is first wet down with gasoline, stirred, and allowed to settle and drain before the test oil is introduced. The first oil through is water white and contains the gasoline, for which an allowance of half the volume of the clay is made. Then follow green, yellow, and red oil, ending with black, unbleached oil. In daylight, the eye is very sensitive to the first green and to the golden yellow, which is between lemon and orange. The recognition of the first red following the orange and the first black is less certain but not difficult with practice.

Thus, four volumes corresponding to the four colors are obtained. The ratios of these oil volumes to the volume of the clay bleaching them are the color indices given in the writer's tests. In practice, the measurement of actual volume is avoided by making clay and oil-drip containers of the same glass tubing and simply comparing the height of clay and oil passed. Thus, a rating of 1.5 means that the oil bleached was 1.5 times the volume of the clay bleaching it. A set of four numbers, such as 1.5, 2.2, 2.8, 3.6, refers to the four colors - water white, green, yellow, and red.

The tubes used for testing are of glass and have an inside diameter of 8 millimeters. (See fig. 10.) A 9-inch piece of tubing is constricted at about one-third its length and cut off. The shorter piece is shaped into a small test tube with slightly flaring top, and the longer piece is formed with a tapered carbon rod to seat a 1/4-inch disk of blotting paper cut with an ordinary file punch. A set of 5 or 6 pairs of such tubes mounted in a frame is convenient for testing. Similar sets of 1-inch metal tubes holding 6 inches of clay and surrounded by a bath of hot oil for controlling temperature have been used in works tests.

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[9] Work cited in footnote 7.

As a test oil, the writer prefers a black, sulfur-free crude oil. This is diluted with gasoline until Floridin clay tests 1.0 to 1.1 for water-white bleach, the complete run being 1.0, 1.3, 1.5, 1.7. Floridin clay is chosen for a reference standard, because it changes little with age. If the test oil is such as to give too low yellow and red separations, these may be increased as desired by adding cylinder stock. A few ounces of 150-mesh clay are kept in reserve for check tests. An advantage of the small glass tubes is the small amount of clay sample required for a test and the small amount of test oil used up; a gallon of test oil is ample for a thousand tests.

Unfortunately, there appears to be no possibility of an absolute method of testing bleaching clays and no escape from the necessity of using reference standard clays and arbitrarily chosen test oils. The substitution of known concentrations of dyes in benzine for test oils has been suggested, but the adsorption of such solutions on clays differs so widely from that of petroleum as to be of little value.

Preliminary tests of clays. - If a clay sample passes inspection as an active or activable clay, about 10 grams are ground to 150 mesh and divided into three portions. One portion is set aside for the test of the bleaching power of the raw clay, and the other two, about 3.5 grams each, are put in 250-cubic-centimeter flasks with 100 cubic centimeters of 1:1 (20 percent) hydrochloric acid and heated to boiling for 1 and 2 hours, respectively, filtered, washed, dried, and sifted. All three samples are then dried at 160° C. for an hour and given the oil test described above. This test is sufficient to determine natural activity and activability. Testing 15 clays in 3 batches of 5 each is a day's work, and several thousand such tests have been made at the Survey.

Color curves. - If a clay shows pronounced activability in the preliminary test, it may be worth a more detailed test to determine the utmost of which it is capable and the precise amount of acid treatment that will give optimum bleach. Five portions of about 3.5 grams each are weighed out of a supply that has been ground to 150 mesh and left overnight to come to room humidity, put in five 250-cubic centimeter flasks with 100 cubic centimeters of hydrochloric acid ranging from 10 to 30 percent in concentration, and heated from about 40 minutes for the 10 percent to 4 hours for the 30 percent. The clay samples are filtered on weighed filter paper, washed and dried, left over night to come again to room humidity, and carefully weighed. Losses in weight should be about 5, 10, 20, 30, and 40 percent, the last residue usually being pure silica. The samples are then ground, dried at 160°, and tested for bleaching power.

Finally, the oil-test results are plotted against percentage removed by acid, and a set of four curves for the four colors is obtained. The lowest curve shows the limit of water-white bleached fraction for different amounts dissolved by acid. This curve usually shows a maximum of 20 to 25 percent removal of soluble material. The effect of low leaches is slight, the action being chiefly an exchange of hydrogen for calcium. When alumina and iron are attacked, the bleaching power rises sharply to a broad optimum. Finally, with overtreatment with acid, the bleaching power drops considerably, to about that of silica gel or fuller's earth. The curves for limiting green, yellow, and red fractions are similar, but with maxima farther to the right, that for the red fraction (petroleum lubricants) being usually at about 30-percent removal of solid materials.

Such sets of color curves are indicative of the nature of the clay, whether or not it has been weathered or kept too long in storage, and show the range of tolerance in plant control. The color curves of most good clays are so flat at their maxima that a departure of 5 percent either way from the optimum leach is of little consequence. A clay being treated for use in bleaching cottonseed, linseed, or palm oil should be slightly undertreated. An overtreated clay is almost valueless.

Work tests. - The tests above outlined are still lacking in the data necessary to establish a formula or recipe for plant operation. Although a 2-hour treatment in 20 percent acid may be best for some clays, for others a 3-hour treatment in 10 percent acid may give better results or be more easily controlled in practice. The data required are obtained by running tests that give sets of solubility curves and making a bleaching test of each portion treated. Weighed samples are digested for 0.5, 1, 2, 3.5, and 5 hours in acid of 1.5, 3.0, 6.0, and 9.0 normality. The four sets of color curves indicate which acid concentration and time of treatment give best results and the range of tolerance in time and concentration.

A quick test to determine the degree of leaching would be valuable in plant control, but no such test is known. To remove a sample from the batch being treated and give it a regular bleaching test would require far more time than is permissible. A sample quickly washed and dried will form a hard cake, if much underdone, but will be incoherent if correctly treated to overdone, but this test is not conclusive. Titration of a sample of spent liquor requires little time but is insensitive on account of the large excess of free acid that is always present. The determination of refractive index requires little time but is not very sensitive. An absorption test on a quickly washed clay sample with a water dye solution would be quick and might be servicable if done by a practiced observer. In the absence of any such quick tests, clay-treating must continue to be by formula alone.

The cracking of oil by clay is not shown by contact methods of testing, but is easily apparent in percolation testing. When the sample of dried clay under test is wet down with gasoline in the regular bleaching test, the top of the clay may turn red, pink, or brown, even though the gasoline used has been treated previously with active clay. Highly purified laxative oil and fused paraffin crack even more readily than gasoline, the longer chain molecules being broken more readily than the shorter ones. Many activated adsorbent clays and some fuller's earths crack gasoline, and there is no way known of preventing it without a considerable sacrifice of adsorbing power, although the addition of chlorinated hydrocarbons is of some assistance. When a bentonite is activated in steps, as for color curves, it is found that maximum cracking occurs at maximum absorbing power and that a fully leached clay shows little or no cracking. Among different clays, cracking and adsorbing power do not always go together.

Note on above test: The test uses a maximum of about 3 grams of clay as a sample. Obviously, a much more representative sample would be of greater size. Also, the tendency to "channel" is quite marked. If one uses a larger sample, say 50 grams, and correspondingly larger tubes (a 100 cc. separatory funnel is excellent), the factor of channeling becomes greater, and there is possibility of some evaporation of the oil-benzol mixture. However, by exercising care, the test works very nicely with samples of as much as 50 grams. With a sample this size, the results of the test are on a par with the cold contact method described in "Contact", second method, above.

One objection to the test is that it requires careful and continuous watching during the hour or more percolation is taking place in order not to miss any of the color changes. Some clays require 3 to 4 hours. Aside from this inconvenience, the method is an excellent one for the clay laboratory.

Colorimeters

As noted in the section on vegetable oils, the American Association of Oil Chemists recommends the Wesson method, using Lovibond glasses, and the Stevenson colorimeter is approved.

For mineral oils, Committee D2, A.S.T.M. on Petroleum Products and Lubricants specifies two colorimeters, the Union colorimeter (A.S.T.M. designation D155-39T) for lubricating oils and the Saybolt chromometer (A.S.T.M. designation D156-38) for light-colored products. These colorimeters depend on matching the oil colors by eye.

Another more recent type is the Hellige-Diller photoelectric colorimeter. This single colorimeter covers the whole range of all the oils and may be run by a color-blind operator. It will be found very satisfactory, particularly for clay laboratories.

It is possible, however, to set up a color evaluation system in a laboratory where a colorimeter is lacking. This can be done by using a standard, high-grade bleaching clay and a standard oil. A series of oil concentrations is then made with the clay, obtaining color shades from water white through greenish-yellow, light amber, medium amber, dark amber, and dark reddish amber to nearly opaque. The shades can be so spaced and plotted against ml. of oil per gram of clay that virtually a straight line results. That is, a constant ratio is arbitrarily set up between ml. of oil per gram of clay and shade. The ordinate or abscissa for the shades can be divided into 30 or 40 divisions, and each shade will cover a number of points of the division, as shown in the bleaching test. This is explained by D. W. Ross in more detail.[10]

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[10] Ross, Donald W., Work cited footnote 6.